

The University of Chicago

ISOMERIZATION AND ESTERIFICATION
OF PINENE

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1936

By

WILLIAM B. REYNOLDS

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

1941

The University of Chicago

ISOMERIZATION AND ESTERIFICATION OF PINENE

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1936

By

WILLIAM B. REYNOLDS

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

1941

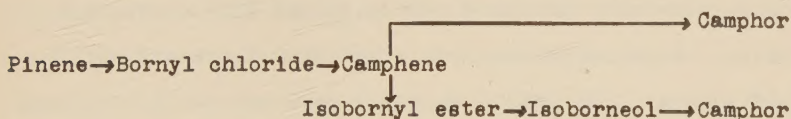
The author wishes to express his
sincere appreciation to Professor
M. S. Kharasch, who directed this work.



ISOMERIZATION AND ESTERIFICATION OF PINENE

INTRODUCTION

Since the Japanese monopoly of the world's supply of natural camphor has made it increasingly difficult to obtain an adequate supply of the natural product, there has been considerable impetus given to the development of a synthetic camphor from more available materials. Two general procedures have found commercial application. The starting product of each is pinene, the chief constituent of oil of turpentine. First, although chronologically a later development, is the scheme represented briefly as follows:



In general the formation of camphor from camphene is accomplished in better yield by the lower branch method. By this procedure about 60 per cent conversion of pinene into camphor is brought about. The second method is the direct action of organic acids on pinene with the formation of esters of borneol. These are saponified and the resulting borneol oxidized to camphor. Although this procedure has the advantage of shortening the number of steps in reaching the final product it has, in general, been characterized by comparatively low yields.

The present work represents a study of the factors influencing the formation of borneol esters by the direct action of organic acids on pinene with particular emphasis upon the nature of the rearrangements involved both in the main reaction and in the formation of various by-products.

HISTORICAL DEVELOPMENT

Near the close of the last century Bouchardat and Lafont¹ observed that when French turpentine oil is mixed with anhydrous formic or acetic acid, the optical activity gradually increases over a period of several months. At 100° the change is much more rapid. Upon careful fractionation of a reaction mixture of pinene and glacial acetic acid, which had been heated at 100° for 137 hours, acetates of terpineol and borneol, in addition to isomerization products of the pinene, were identified. Later, the same investigators² studied the products formed when molecular quantities of pinene and benzoic acid were heated at 150°. Qualitatively, the products were very similar to those formed with acetic and formic acids. From 1- α -pinene they identified 1-borneol and d-isoborneol esters. Similarly d- α -pinene gave esters of d-borneol and 1-isoborneol.

Since this early work a large variety of acids, catalysts, and solvents has been used in attempts to increase the yields of borneol esters and decrease the isomerization to monocyclic terpenes. Since most of this work has been industrial research it is reported largely in the patent literature. Several acids have been found to give reasonably good yields of borneol esters³ in the absence of solvents and catalyst. Among these should be mentioned salicylic, tetrahalophthalic, and acids of the general

¹Ann. chim., (6), 9, 507 (1886); 15, 145, 149, 166, 185 (1892).

²Bouchardat and Lafont, Compt. rend., 113, 551 (1891); Bouchardat and Tardy, ibid., 120, 1417 (1895).

³Or borneols, since saponification is efficient.

type COOH-R-CO-R' , where R and R' represent aromatic nuclei, exemplified by o-benzoyl benzoic acid.

Salicylic acid was first reported in this reaction by Tardy.¹ Later Duboso and Luttringer² reported the preparation of borneol esters from pinene and salicylic acid. According to their method the esters were oxidized directly to camphor by alkaline peroxides. Mulany and Watson³ report a 70 per cent esterification of pinene by two parts of salicylic acid at 150° . The esters obtained by them, upon saponification gave a semi solid mass, which the later work of Delepine, Reisman, and Suau⁴ definitely shows to be a mixture of borneol, isoborneol, and fenchol. In 1927 Austerweil⁵ studied the action of salicylic acid on both alpha and beta pinene. Qualitatively the products were similar although according to the reasoning of Austerweil the alcohol from beta-pinene contained considerable quantities of isoborneol while that from alpha-pinene was almost pure borneol. The work of Delepine, Reisman, and Suau, which has already been mentioned, points out the fallacy of Austerweil's conclusion that alpha-pinene, with salicylic acid, gives pure borneol.

The use of tetrachlorophthalic acid was developed by Haller for Fabriques de Produits Chimiques de Thann et de Mulhouse.⁶ The original patent reports about 20 per cent con-

¹Journ. Ph. et Chim., (6), 20, 57 (1904).

²Bull. soc. ind. Rouen, 48, 85 (1920).

³J. Indian Chem. Soc., 3, 253 (1926).

⁴Bull. soc. chim., 47, 966 (1930).

⁵Bull. soc. chim., 41, 1507 (1927).

⁶Haller, Compt. rend., 178, 1933 (1924); British Patents 144,604; 158,533; United States Patents 1,415,340; 1,429,342.

version of pinene into borneol. Later the use of organic solvents was reported to have considerably improved the yields.

In 1927 the use of ketonic acids of the type COOH-R-CO-R' "wherein R and R' represent aromatic nuclei, their homologues or substitution products" was patented in the United States by H. Blum for Societe Alsaciens de Produits Chimiques.¹ This patent claims yields of as high as 80 per cent of borneol from pinene. However, work in this laboratory as well as the results of Delephine, Reisman, and Suau² indicates that the percentage conversion is appreciably lower than the patent claim. According to patent specifications the acid is heated with an excess of pinene. At the end of the reaction the excess terpene is removed and is claimed to remain substantially unchanged. Delephine, Reisman, and Suau found the excess terpene to contain not more than 50 per cent pinene.

Reports of yields with anhydrous oxalic acid vary from ten to thirty per cent conversion.³ Yields with oxalic acid are appreciably increased by the use of solvents and catalysts, notably certain chlorinated hydrocarbons.⁴

A few other acids are mentioned in the literature in connection with this reaction. In most cases the data on yields are either lacking or inconclusive. Darrasse⁵ mentions sebacic acid; Delephine, Reisman, and Suau worked with mono- and dichloroacetic

¹Blum, United States Patent 1,640,639; cf. French Patent 592,213.

²Op. cit., p. 976.

³Murayamo and Abe, J. Pharm. Soc. Japan, No. 498, 637 (1923).

⁴Darrasse and Darrasse, British Patent 164,357 (1921); French Patents 393,478 (1908); 528,455 (1910).

⁵Darrasse and Darrasse, British Patent 164,357 (June 6, 1921); French Patents 393,478, 528,445.

acids, while Murayamo and Abe¹ report the use of trichloroacetic, tartaric, and citric acids. The latter two were entirely unsuccessful. Picric acid has been found to give bornyl picrate when heated with pinene.² In all of these cases the large amounts of by-products make the acids undesirable for the preparation of borneol. The chief side product of the esterification is fenchyl alcohol, while limonene predominates in the unesterified terpene mixture.

RELATION OF STRENGTH OF ACID TO BORNEOL YIELD

Correlations between the tendency of acids to form borneol esters with pinene and other properties of the acids are almost entirely lacking in the literature. Haller³ mentions that tetrachlorophthalic acid was used "because it is exempt from Viktor Meyer's Law of steric hindrance."⁴ However, since the esterification of pinene is not analogous to the esterifications described by Meyer and since later work shows a number of ortho substituted acids (e.g., ortho benzoyl benzoic) to give good yields of ester it is apparent that no evidence exists for steric influence.

Delepine, Reisman, and Suau⁵ have observed that the reactivities of acids toward pinene are roughly proportional to the ionization constants of the acids. As evidence they submit the following conditions necessary for various acids to react with pinene:

¹Op. cit., p. 638.

²Lextreit, Compt. rend., 102, 555 (1886).

³British Patent 144,604 (1919); 18,049 (1908). Compt. rend., 178, 1933 (1924).

⁴Meyer, Ber., 28, 182, 1254 (1895).

⁵Op. cit., p. 966.

TABLE I

Acid	Ionization Constant	Conditions for Reaction
HCl.....	0.8	Combines on contact
H ₂ SO ₄	0.8	Combines on contact
Cl ₃ C-COOH.....	0.3	Combines rapidly but more slowly than two above
Picric.....	0.16	Requires several minutes at 150°; $\frac{1}{2}$ hr. at 120°
Oxalic.....	0.038	Several hrs. at 140°
Tetra chloro phthalic	0.025	30 hrs. at 100-105°
Salicylic.....	0.0011	50 hrs. at 130-35°
o-Benzyl benzoic....	0.00037	50 hrs. at 140°
Benzoic.....	0.000058	30 hrs. at 145-50°
Acetic.....	0.000018	60 hrs. at 100°

On the basis of the table they were able to predict the temperature and time necessary for mono and dichloro acetic acids to react with pinene.

Since the above tabulation merely represents the destruction of pinene by acids and not the amount converted into borneol esters it seemed desirable to study the effect of acid strength upon the quantity of pinene converted into borneol. For this study monobasic organic acids, having ionization constants between 0.3 and 350×10^{-4} at 25°, were selected. All of the acids were miscible with pinene in the proportions used at the reaction temperature. In all cases 0.18 mol of acid was heated with 0.38 mols of pinene on an oil bath at 135-40° for forty-three hours. The excess terpene was removed by steam distillation and the residual ester saponified with excess alkali. The borneol was removed from the saponification mixture by steam distillation and worked on a

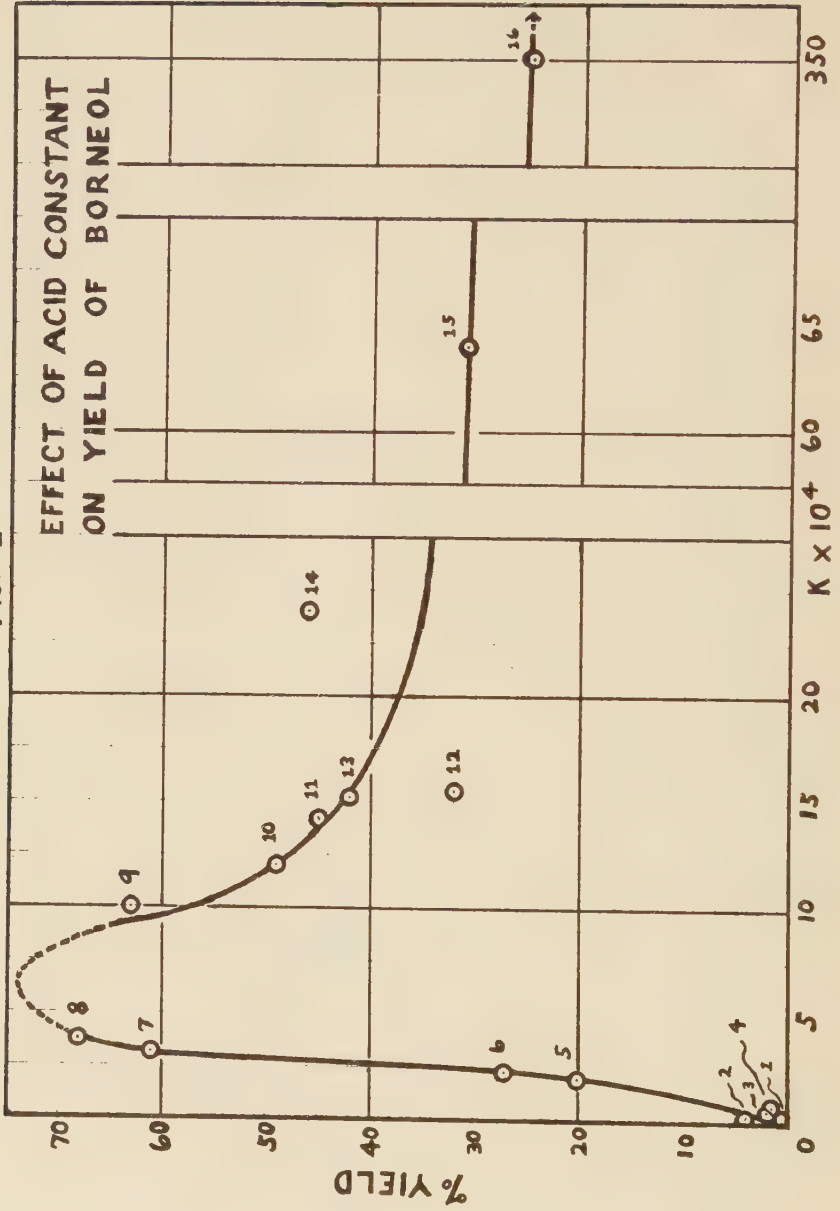
suction filter to remove traces of terpene and fenchyl alcohol. The yields are calculated on the amount of acid used and represent the crude product as described, which is a mixture of borneol with smaller quantities of isoborneol.

TABLE II

Acid	No. Fig. I	K x 10 ⁴ (25°)	Yield of Borneols
p-Methoxybenzoic.....	1	0.3	per cent 0.5
Cinnamic.....	2	0.36	4.
Benzoic.....	3	0.58	2.
o-Methoxybenzoic.....	4	0.8	1.5
Alpha-naphthoic.....	5	2.	20.
Ethoxyacetic.....	6	2.3	27.
m-Nitrobenzoic.....	7	3.16	61.
o-Benzoylbenzoic.....	8	3.7	68.
Salicylic.....	9	10.	63.
o-Chlorobenzoic.....	10	12.	49.
o-Bromobenzoic.....	11	14.2	45.
3,5-Dinitro benzoic...	12	15.5	32.
Chloracetic.....	13	15.2	42.
5-Bromosalicylic.....	14	24.	46.
o-Nitrobenzoic.....	15	64.	31.
2,4-Dinitrobenzoic....	16	350.	27.
Trichloroacetic.....	17	Very strong	25.

In Figure I the yields are plotted against the acid constants. The maximum would appear to lie between $K = 3.7$ and 8×10^{-4} .

FIG. 1



The highest possible yield of borneol with the quantities used in the experiments would probably be less than 80 or 85 per cent. This is true probably because the conditions bringing about esterification invariably cause isomerization of a part of the pinene to limonene. The relation between these two courses of the reaction will be discussed later.

ACTION OF BENZOIC ACID ON PINENE-
EFFECT OF SOLVENTS

Since benzoic acid alone with pinene, under the conditions of the experiments above, gave very low yields of borneol it was felt that a study of factors increasing the yield with that acid should give valuable information about the course of the reaction.

d- α -Pinene is thermally stable at 140° A sample heated in an evacuated, sealed tube in an oil bath at 140° for 201 hours was unchanged in boiling point, optical rotation, and refractive index. At 200° the results of Conant and Carlson¹ and others² have been confirmed in this laboratory. The loss of optical activity is quite rapid, due to the isomerization of the pinene to inactive dipentene. Since esterification and isomerization of pinene seemed to be closely related it was felt that a condition bringing about isomerization (i.e., temperature of 200°) might also facilitate esterification. This was indeed found to be the case. Sixty cubic centimeters of pinene with 24.4 grams of benzoic acid in an evacuated, sealed tube heated at 200° for forty-one hours gave 25 grams of a fraction distilling from 150-63° at 5 mm. pressure. Bornyl benzoate prepared from borneol and benzoyl chloride boiled at 158-9½° (uncor.) at 5 mm. pressure. The above

¹J. Am. Chem. Soc., 51, 3464 (1929).

²Smith, ibid., 49, 43 (1927); Thurber and Johnson, ibid., 52, 786 (1930).

fraction, when saponified with alcoholic potassium hydroxide gave 12 grams of a pasty solid. This paste, upon distillation, gave 9 grams of a solid mixture of borneol and isoborneol or a yield in excess of 30 per cent as compared with 2 per cent at 140° . It should be remarked here that two factors probably influence the increased yield at the higher temperature. First, the pinene is activated as is indicated by thermal isomerization to dipentene. Second, it is to be expected that an acid such as benzoic, which is weaker than the optimum strength at 140° as indicated by Figure I, would be more effective at a higher temperature where its acid strength would be enhanced. This would imply also that acids, which at 140° are of optimum strength or stronger, would be less effective at more elevated temperatures. This has been found to be true.

Since benzoic is a weaker acid than the optimum indicated by Figure I, it might be expected that increasing the dielectric constant of the reaction mixture would also increase the yield of borneol. It should be borne in mind that since the isomerization of pinene is monomolecular and the esterification bimolecular,¹ the addition of any solvent would, through dilution, favor the former. Hence one should not expect, on the basis of raising the dielectric constant alone, to obtain yields with benzoic acid comparable with those of optimum strength acids heated alone with pinene.

In the following runs 0.2 mol of benzoic acid plus 0.2 mol of solvent were heated with 0.38 mol of pinene for 43 hours at $135-40^{\circ}$. The reaction mixtures were worked up for borneol as previously described. Saponification of the esters was with alcoholic potassium hydroxide. Yields are based on the amount of

¹Austerweil, Bull. soc. chim., 41, 1088 (1927).

acid used. The results are summarized in the following table:

TABLE III

Solvent	Yield of Borneol per cent	k(dielectric) of Pure Solvent
Anisole.....	2.	4.3 (20°)
Nitrobenzene.....	3.	36. (20°)
Quinoline.....	5.	9. (20°)
Catechol.....	22.	
o-Cresol.....	23.	8. (40°)
p-Nitro phenol.....	27.	
Resorcinol.....	28.	3.2 (22°)
Beta-naphthol.....	34.	
Phenol.....	32.	4.3 (10°)
p-Cresol.....	36.	13. (40°)
m-Cresol.....	40.	13. (40°)
Benzonitrile.....	9.	26. (20°)

Since the solvent effect of phenolic compounds is marked and certainly not to be accounted for on the basis of dielectric constants, an explanation of their action is to be sought in another direction. According to Lextreit¹ picric acid reacts with pinene to give a small amount of bornyl picrate. In the reaction mixture was found camphene in addition to numerous by-products. The camphene probably resulted from the breakdown of part of the bornyl picrate. Much later Kondakov² studied the reaction of l-pinene from French turpentine oil with a large number

¹Op. cit., p. 555.

²Parfumerie moderne, 19, 212 (1926).

of substituted phenols. He reports appreciable quantities of that pinene, which contains appreciable quantities of beta-pinene, to be isomerized to camphene by the phenols. With mononitro-phenols 20 per cent of the pinene was converted into camphene. The use of phenols for converting pinene into camphene is covered by a French patent.¹ Since camphene is known to esterify readily, it at first appeared probable that the function of the phenols was to isomerize the pinene to camphene, which was then esterified by the acid. Two considerations, however, lead to the discard of such an explanation. First, experiments upon the action of phenol and m-cresol on d- α -pinene indicate that isomerization of pinene to camphene does not occur to any considerable extent under the conditions of our runs. Pinene in evacuated, sealed tubes was heated at 140° with 10 mol per cent of phenol. At the end of 60 hours the rotation and refractive index of the solution was unchanged. Pinene, heated similarly with m-cresol, was unchanged after 179 hours' heating.

In the second place the character of the products formed in the runs using phenolic solvents precluded their formation by the esterification of camphene. Camphene, with organic acids, leads almost exclusively to the formation of isobornyl esters. Saponification of these esters gives isoborneol, which may be optically inactive or possess a rotation opposite to that of the camphene used.² It is now evident that a determination of the amount of isoborneol in the solid alcohols obtained from the phenol runs would indicate whether the bulk of the product was ob-

¹French Patent 545,368 (1910).

²A sample of camphene having a specific rotation of 34.7° (3 g. in 25 cc. absolute alcohol) gave with benzoyl benzoic acid an isoborneol having $[\alpha]_D -4.16^\circ$ (1.5 g. in 25 cc. alc.).

tained by direct esterification of the pinene or by the esterification of camphene formed as an intermediate. The observation of Haller¹ that the specific rotation of isoborneol is nearly twice as great in alcohol as in toluene while the rotation of borneol is approximately the same in the two solvents was used by Austerweil² in estimating the percentage of mixtures of d-borneol and l-isoborneol in samples obtained by esterifying pinenes. His method was criticized by Delepine, Reisman, and Suau³ on the grounds that it would only be accurate if the components of the mixture were optically pure. As this would never be true of alcohols obtained from pinene, since the pinene varies considerably in optical purity depending upon its source, Delepine, Reisman, and Suau applied a correction factor to the Haller-Austerweil method. Both d-borneol and l-isoborneol oxidize to d-camphor. By oxidizing a mixture of the two their percentage optical purity can be determined by the ratio of the rotation of the camphor obtained to the rotation of pure d-camphor. By utilizing the following known values:

$$\left. \begin{array}{l} [\alpha]_D \text{ for d-borneol} = 37.33^\circ \\ [\alpha]_D \text{ for l-isoborneol} = -32.9^\circ \end{array} \right\} \text{ in absolute alcohol}$$

$$\left. \begin{array}{l} [\alpha]_D' \text{ for d-borneol} = 37.87^\circ \\ [\alpha]_D' \text{ for l-isoborneol} = -18.93^\circ \end{array} \right\} \text{ in toluene}$$

$$[\alpha]_D \text{ for d-camphor} = 43.15^\circ \text{ in absolute alcohol}$$

and measuring the rotations of the alcohol mixture both in alcohol and in toluene as well as the rotation of the camphor to which the mixture oxidizes, Delepine, Reisman, and Suau give the fraction of isoborneol in a mixture by:

$$x = \frac{(37.33)(p) - [\alpha]_D}{(70.23)(p)} \quad \text{or} \quad x' = \frac{(37.87)(p) - [\alpha]_D'}{(56.80)(p)}$$

¹Comp. rend., 109, 187 (1892).

²Op. cit., p. 1088.

³Op. cit., p. 967.

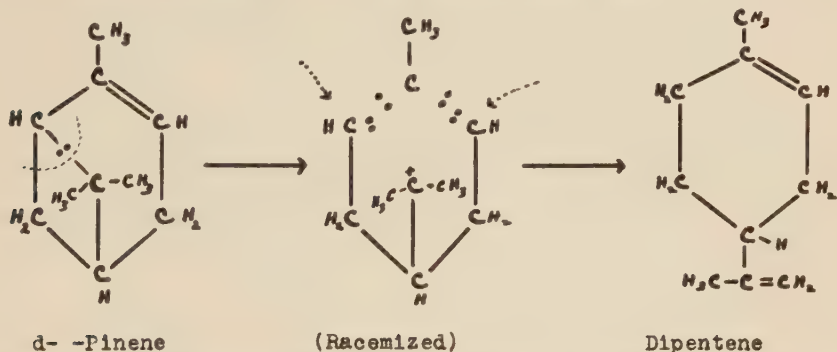
where p is the fraction of optical purity and $[\alpha]_p$ and $[\alpha]_t$ are the rotations of the alcohol mixture in alcohol and toluene.

A sample of the crude borneol obtained from pinene with benzoic acid and cresol had a specific rotation of 18.8° in alcohol (1.5 g./25 cc.) and 20.2° in toluene (1.5/25) while upon oxidation with nitric acid it gave a camphor having 25.2° (1 g./25 cc. alcohol). From this value $p = 25.2/43.15 = 0.584$ and $X = 0.07$ while $X' = 0.06$. Obviously less than 10 per cent of the crude sample was isoborneol. Since the direct action of acids on pinene leads to the formation of comparable amounts of isoborneol, it seems definitely disproved that the increased yields brought about by phenols are due to intermediate isomerization to camphene. The effect is doubtless due to the increased availability of hydrogen ion as will be more fully discussed later. It should be noted that acids near the optimum strength (e.g., salicylic and m-nitro benzoic) are less effective in the presence of cresols. Probably in these cases dilution, favoring the monomolecular isomerization, offsets the "phenol effect" which would be small for acids of near optimum strength.

MECHANISM OF THE REACTION

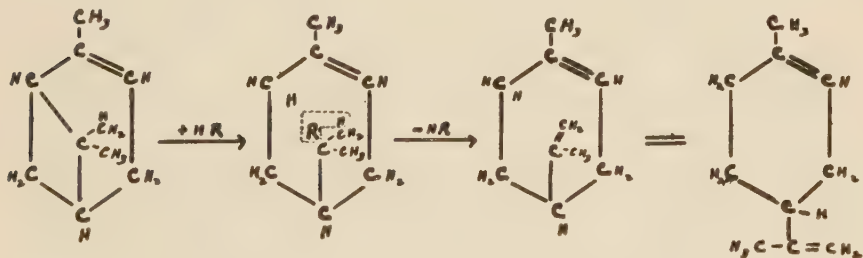
Until Wagner and Meerwein pointed out the analogy between rearrangements in the terpene series and the well known pinacol-pinacol-in rearrangement, there seemed to be no order in the many complex terpene rearrangements. Now upon the basis of their work it is possible to understand why pinene should react with organic acids to give a mixture of bornyl, isobornyl, and fenchyl esters together with limonene and other isomerization products. As was remarked earlier, pinene isomerizes thermally to give inactive dipentene. In the presence of hydrogen ion it isomerizes to

limonene, the active form of dipentene. To explain why inactive dipentene is formed in one case and limonene in the other it is desirable to postulate different points of attack in the molecule. Thermally the break is likely to occur where there is most strain in the pinene molecule, i.e., the cyclo butane ring:



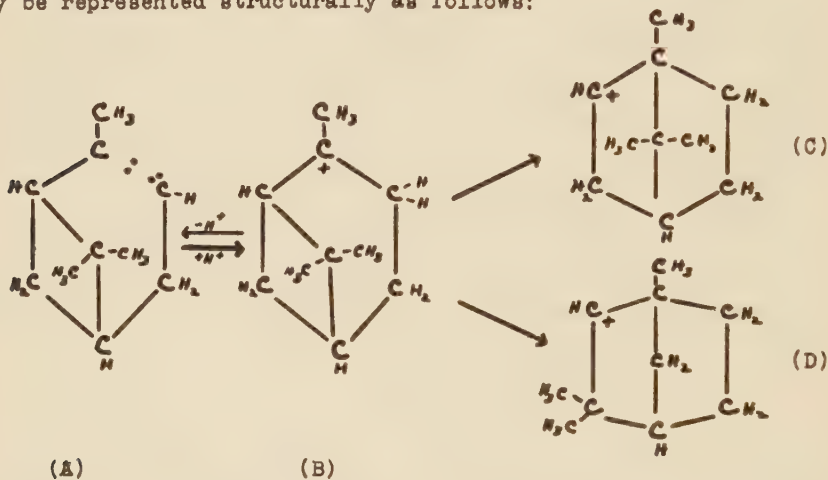
After the cleavage indicated by the dotted line above, the molecule becomes symmetrical. The hydrogen from the isopropyl carbon can then stabilize the molecule by migrating to either of the two carbon atoms indicated, resulting in the formation of dipentene.

For the acid catalyzed isomerization Austerweil¹ has also chosen the cyclobutane ring as the point of attack. His mechanism is represented as follows:



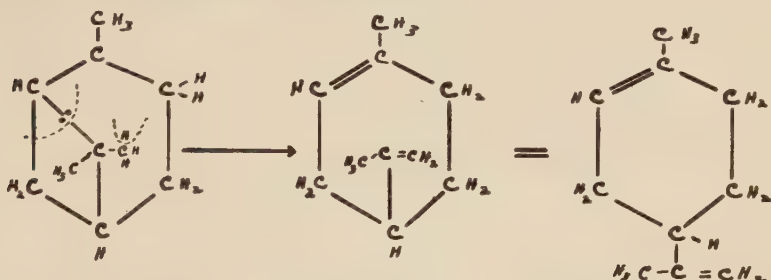
¹Bull. soc. chim., 39, 1732 (1926).

Since it was observed that organic acid-catalysed isomerization to limonene was invariably brought about under conditions leading to esterification it seemed expedient to regard the isomerization and esterification as parts of a single mechanism and to postulate the double bond as the point of attack. Accordingly, the first step in either reaction is the capture of a hydrogen ion, leaving a positive charge on the carbon atom holding the methyl group. Since this is the typical unstable ion of the pinacol-pinacolin rearrangement, it is to be expected that the ion should stabilize itself by migration of one of the bonds of the cyclobutane ring to the positive carbon atom holding the methyl group. These steps may be represented structurally as follows:



The addition of the acid radical to the ion (C) gives an ester of borneol or isoborneol, depending upon whether the addition occurs cis or trans to the isopropyl group, while the addition to the ion (D) gives an ester of fenchyl alcohol. Since fenchyl esters are formed in rather small quantities in this reaction the formation of (C) is evidently favored over the rearrangement to (D). The amount of fenchyl ester formed varies somewhat with reaction conditions and acid used.

Now returning to the formation of active limonene it is observed that either (B) or (C) in the scheme above can stabilize by eliminating a hydrogen ion. (B) can lose the same proton originally captured so the first step should be represented as an equilibrium. Or, it can eliminate a proton from the isopropyl group with the formation of limonene:



Obviously the same thing might happen to (C) so there is no way of telling definitely whether the break occurs before or after the rearrangement.

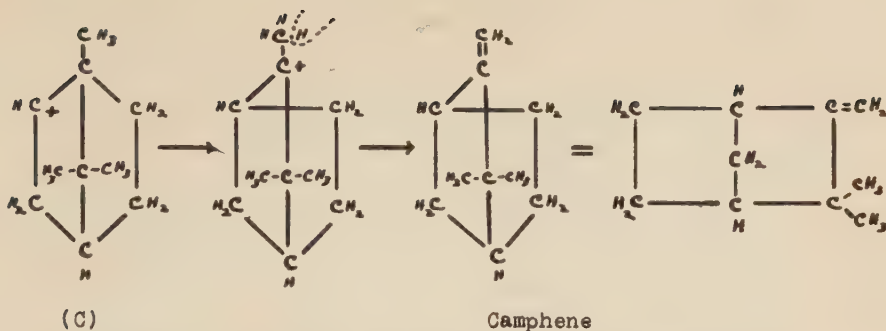
Although d-limonene is invariably formed simultaneously with the esterification of pinene by acids, indicating that limonene formation is catalysed by a "proton donor," more conclusive evidence would be furnished if it were possible to obtain limonene under conditions which would reduce or eliminate esterification. A clue to such a possibility was furnished by the fact that when formamide was added to a run with benzoic acid and pinene the excess terpene contained a large amount of limonene, indicated by increased boiling point and optical activity (observed rotation in a two-decimeter tube increased from 51 to 66° while over 40 per cent boiled between 170 and 180°). Accordingly, two cubic centimeters of formamide were added to a run of salicylic acid and pinene. The yield of borneol was reduced from 63 to 28 per cent while practically all of the excess terpene boiled between 170-78°. When acetamide in molar quantities with the

acid was added to a similar run, the yield was reduced to 19 per cent. Over 80 per cent of the excess terpene boiled between 170-80° and the observed activity in a two-decimeter tube had increased from 51 to 67°. More striking is the result of formamide added to a run of benzoylbenzoic acid with pinene. No borneol was formed; yet the excess terpene was very much more isomerized than in a run without the formamide. Check runs of pinene with formamide and acetamide showed that the increased isomerization was not caused by the amides alone.

Cutting down the availability of hydrogen ion resulted, as was to be expected, in a decrease both in the esterification and in the isomerization. Salicylic acid and pyridine in equimolecular quantities were heated with pinene under the usual conditions. Only 10 per cent of borneol was obtained from the run while the excess terpene fraction was over 60 per cent unchanged pinene.

Pinene heated with potassium benzoate under the usual conditions was unchanged. These considerations indicate clearly that both courses of the reaction are initiated by a proton donor.

It is felt that the mechanism postulated represents more nearly the true picture of the esterification of pinene than does the formation of a tertiary ester by direct addition to the double bond. In the first place the mechanism advanced explains why phenolic compounds increase the amount of esterification, i.e., by favoring the formation of (B) and (C). That phenolic compounds actually can bring about the rearrangement in the same way as acids is evidenced both by the formation of bornyl picrate from pinene and picric acid and by the isomerization of pinene to camphene by phenols. In the absence of an acid ion (C) might rearrange and eliminate a proton as follows:



This, indeed, is the essential part of the mechanism given by Meerwein¹ for the dehydration of borneol or isoborneol to camphene.

Besides not explaining the phenol effect, a mechanism of direct addition to the double-bond is not logical upon other grounds. Although true pinene hydrochloride is known and can be obtained by the action of hydrogen chloride on pinene, it is very unstable and rearranges at ordinary temperatures to bornyl chloride. The tertiary organic ester probably would be unstable also, especially at the reaction temperature. To test whether or not benzoylbenzoic acid might be expected to add directly to a double bond such as that in pinene, it was heated with a variety of unsaturated compounds. Of the following compounds the acid esterified only the first two: (1) pinene, (2) camphene, (3) ethyl maleate, (4) ethyl fumarate, (5) trimethylethylene, (6) cyclohexene, (7) 1-methyl cyclohexene. In none of the last four cases could enough ester be isolated for identification. The case of methylcyclohexene particularly demonstrates that the esterification of pinene is not brought about by direct addition of acid to the double bond.

It has also been proved that the isomerized terpenes of the reaction mixture are not formed by breakdown of the borneol

¹Ann. 405, 129 (1914).

esters, i.e., the esters are not in equilibrium with other components of the reaction mixture. To prove that the esters, once formed, are stable under the conditions of the reaction, the borneol esters of benzoyl benzoic and benzoic acids were isolated and their stability studied.

Bornyl benzoylbenzoate was prepared by heating o-benzoylbenzoic acid with an excess of pinene at 140° for 35 hours. The excess terpene was removed by vacuum distillation and finally by prolonged steam distillation. An ether solution of the residue was then extracted with carbonate solution to remove unchanged acid. The ether solution was then washed with water, dried and the ether removed. The ester was a clear viscous syrup which resisted crystallization. Saponification of a sample gave 98 per cent of the theoretical amount of borneol. Another sample of the ester was heated for 45 hours at 140° with 90 mol per cent of pinene. The pinene was removed by steam distillation and found to be unchanged, while saponification of the remaining ester gave 98½ per cent of borneol. Obviously the ester is stable in pinene solution at 140° .

Bornyl benzoate was prepared by heating borneol with benzoyl chloride at 150° until the evolution of hydrogen chloride ceased. The reaction mixture was fractionated at 5 mm. pressure where the bornyl benzoate distilled at $158-60^{\circ}$. A sample heated with pinene as above led to the recovery of 98 per cent borneol while the pinene was unchanged.

In view of the evidence presented in the preceding pages it is felt that the mechanisms postulated represent most satisfactorily the courses of the reactions involved.

SUMMARY

1. The effect of acid strength upon the yields of borneol from pinene and monobasic organic acids has been studied.

2. The effect of solvents, particularly phenolic substances, upon the reaction between pinene and organic acids has been studied.

3. The products of the reaction have been studied and a mechanism for their formation suggested, which is based upon:

- a. The effect of hydrogen ion.
- b. The thermal isomerization of pinene to dipentene and catalytic isomerization to limonene.
- c. The close relation of the esterification and catalytic isomerization.
- d. The non-esterification of methyl cyclohexene by o-benzoyl benzoic acid.
- e. The stability of bornyl esters in pinene solution at the reaction temperature.
- f. The general theory of the Wagner-Meerwein rearrangements.

